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Distribution Category UC-63

LOW COST SILICON SOLAR ARRAY PROJECT

SILICON MATERIALS TASK

DEVELOPMENT OF A PROCESS FOR HIGH CAPACITY ARC HEATER PRODUCTION OF SILICON FOR SOLAR ARRAYS

Contract No. 954589

Quarterly Technical Report July-September, 1977

Maurice G. Fey, Program Manager

Westinghouse Electric Corporation
Power Circuit Breaker Division
Trafford, Pennsylvania 15085

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS 7-100 for the U. S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

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Approved:

Maurice G. Fey
Program Manager

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1. INTRODUCTION

1.1 Program Description and Objectives

A program has been established at Westinghouse to develop a high temperature silicon production process using existing electric arc heater technology. Silicon tetrachloride and a reductant will be injected into an arc heated mixture of hydrogen and argon. Under these high temperature conditions, a very rapid reaction is expected to occur and proceed essentially to completion, yielding silicon and gaseous sodium chloride. Techniques for high temperature separation and collection of the molten silicon will be developed using standard engineering approaches, and the salt vapor will later be electrolytically separated into its elemental constituents for recycle. Preliminary technical evaluations and economic projections indicate not only that this process appears to be feasible, but that it also has the advantages of rapid, high capacity production of good quality molten silicon at a nominal cost.[1]

As currently envisioned, the Westinghouse program consists of a four-phase effort directed to the development and implementation of this technology. The initial phase of the program, Phase I, was an eleven-month study funded by JPL which was completed during the quarter. While the overall program objective is to produce 1000 metric tons of high quality silicon per year on a continuous basis, Phase I was defined as a comprehensive feasibility and engineering review of the reaction process, and a formulation of the design for a test system to experimentally verify the high temperature reaction.

Phase II, currently underway, involves a detailed engineering analysis of the entire process, as well as the actual experimental reduction of silicon tetrachloride to yield silicon on a batch basis, at rates of approximately 100 Kg per one hour test. Phases III and IV of the program will focus on the design, construction, and operation of a development facility for the overall process and a commercial size demonstration plant, respectively.

Phase I of the project was organized into a four-task structure conducted during the initial eleven-month phase of the program. In late April 1977, a contract modification was received from JPL which initiated the additional task (Task 5) of Phase II. The objectives of Task 5 are summarized below. Its objective is to establish the practicality of incorporating an arc heater process for the reduction of silicon tetrachloride to produce high purity silicon. The individual objectives of the five tasks of the program are defined as follows:

TASK 1: Reaction Analyses - Perform thermochemical analyses employing free energy minimization to obtain the conditions for maximum yields of silicon based on the use of hydrogen, sodium, magnesium, or zinc as the reductant. Select the optimum reductant for the $SiCl_4$ reactant.

TASK 2: Plasma Reactor Preparation - Develop a design for the plasma reactor and define operating parameters based on the use of arc heaters.

TASK 3: Reactant Storage and Injection - Formulate designs for the reactant storage and injection systems.

TASK 4: Product Collection and Effluent Disposal - Analyze and design a technique for collecting the molten silicon product and develop a means for disposal of the effluent gases (by-products).

TASK 5: Process Engineering Analysis and Design Review - Conduct a detailed process engineering analysis for the entire recycle process for silicon production including design reviews and costing information for the Phase II experimental verification testing.

2. PROGRAM SUMMARY

During the quarter, work continued on the Task 5 effort. Major emphasis was focused on obtaining price data for the various system components required for a plant that produces 1000 MT/year of silicon based on a recycle scheme. This data will serve as the basis for the economic analysis for 1000 MT of silicon per year production.

Work continued on the System Purity analysis which will predict the maximum allowable impurities in the feedstocks ($SiCl_4$ and sodium) based on a desired purity of the silicon product. The computer program, CHEMEQ, has been modified for this purity analysis. Also, the activity coefficients of Fe, Cr, Mn, and Aℓ in liquid silicon at several temperatures have been obtained. These are the metallic impurities in silicon that are being considered for the purity analysis along with Ti and V. Estimation of values for the activity coefficients for Ti and V in liquid silicon is still in progress.

System components and cost information have been assembled for the $SiCl_4$ feed system, sodium feed system, plasma reactor/separator system, and the silicon collection system. This data is being factored into the capital equipment costs for the economic analysis for the 1000 MT of Si/year case.

Effort was continued to specify and assemble cost information for the NaCl electrolysis system that is necessary for the recycle process envisioned to produce 1000 MT of silicon/year. Base case conditions and analysis assumptions were made in addition to data gathering from literature sources. The three primary producers of sodium in the United States have been contacted to solicit operating information regarding the electrolysis of NaCℓ. However, the amount of information received to date has been minimal, due to proprietary information concerns by the sodium producers. Further discussions with the producers are continuing. A preliminary flowsheet for the NaCℓ electrolysis process was assembled.

A number of $SiCl_4$ producers have been identified and surveyed to solicit information on $SiCl_4$ price and purity. These producers can be categorized into two main groups: (1) production of $SiCl_4$ as a main (direct) product and (2) production of $SiCl_4$ as a by-product of some other process (e.g., $SiCl_4$ is produced as a by-product from the $ZrCl_4$ process). Of the direct $SiCl_4$ producers, i.e. Van DeMark Chemical Co. and Cabot Corp., detailed operating information was obtained from Van DeMark only. A request to Cabot Corp. was made for process and operating information; however, proprietary information concerns have restricted any information transfer. Information channels are being maintained with Cabot in order to obtain the $SiCl_4$ process information if it becomes available.

As a result of a meeting with Van DeMark Chemical Co., a preliminary process design analysis for $SiCl_4$ production based on chlorination of silicon carbide has been completed. This analysis yielded a listing of major process equipment and sizes from which equipment costs will be determined and factored into the economic analysis for producing 1000 MT/year of silicon.

Additional thermochemical computer analyses were conducted for the chlorination of SiC and for the chlorination of SiO_2-C mixtures to determine theoretical materials and energy requirements and are presented in Section 3.7.

An analysis is being conducted by CYM Engineering Co. to determine the requirements for $SiCl_4$ purification via distillation based on a Van DeMark $SiCl_4$ feedstock. Three separate cases are being analyzed by CYM, and present designs for varying degrees of purification for the $SiCl_4$ feedstock. To date two cases have been completed and the reports submitted to Westinghouse. These reports present: (1) base case conditions, (2) preliminary flowsheet, (3) preliminary materials and energy requirements, and (4) a list of major process equipment including cost estimates. The third case analysis is still in progress.

Continued analysis and design of the effluent separation system via a salt (NaCl) cyclone technique has been pursued. The salt cyclone employs additional NaCℓ(s) injection into the effluent gas stream which contains $NaCl_{(v)}$, Ar, and H_2 from the reduction reaction, and this injected $NaCl_{(s)}$ cools and quenches the $NaCl_{(v)}$ to aid nucleation separation of the salt from the gases. The resulting $NaCl_{(\ell)}$ is collected in a water-cooled vessel. Component design and sizing for the NaCl cyclone have been performed. In addition, heat transfer calculations have been made to predict the equilibrium wall thickness of liquid salt that lines the cyclone walls. Since the effluent gases (Ar and H_2) will pass through a gas scrubber after the salt cyclone and prior to the gas burnoff stack, a calculation was performed to determine the rate of water vapor diffusion upstream of the scrubber as regards potential system contamination. The results of this analysis are presented with the conclusion that water vapor contamination by diffusion cannot occur under normal operating conditions.

Work has continued on assembling the economic data for analysis to estimate the $/kg of Si based on producing 1000 MT/year.

During the upcoming quarter, major emphasis will include: (1) completion of the 1000 MT/year economic analysis, (2) additional design analysis of the effluent separation system, and (3) conducting a design review of the Task 5 effort with JPL personnel.

a two-phase liquid plus solid solution forms below an aluminum mole fraction, $x_{A\ell}$, of 0.65. The extrapolation of these data to the desired temperature range requires two assumptions. The measured value of the alpha function, i.e.

$$\alpha_{A\ell} = \frac{\ln\gamma_{A\ell}}{(1-x_{A\ell})^2}$$

which is constant for $0.65 \leq x_{Al} \leq 0.90$, applies to hypothetical, super-cooled liquid silicon alloys with aluminum compositions below 0.65. Secondly, silicon rich, liquid Si-Aℓ alloys form regular solutions, i.e. the entropy of solution is ideal. The calculated activity coefficients are shown in Table 1. The activity coefficient is less than one in all cases indicating negative deviations from ideality. On this basis, it is probably reasonable to assume that other metallic solutes in liquid silicon, such as Ti and V, for which activity data are not available, exhibit negative deviations from ideality. Consequently, in future calculations for the metallic impurities for which measured activity coefficients are not available, negative deviations from ideality will be assumed.

The equilibrium composition of liquid silicon produced by the arc heater reduction of $SiCl_4$, by either sodium or hydrogen, will be calculated as a function of initial impurity level in the feedstock for Fe, Mn and Aℓ and Cr impurities. The base conditions for these calculations are an initial $Na/SiCl_4$ ratio of 4.05, i.e. the optimum yield ratio, a temperature of 1900°K, and impurity levels in the range between 1 and 1000 ppm of initial $SiCl_4$. The effect of temperature and the initial $Na/SiCl_4$ ratio will be determined.

Table 3.1 - Activity Coefficients in Liquid Silicon at Infinite Dilution

Elements	Activity Coefficient, γ_i°				Temperature of Measurement (°K)	Reference (See Below)
	1700°K	1900°K	2100°K	2200°K		
Iron	.0132	.0178	.0335	.0440	1873	A
Chromium	.0111	.0180	.0300	.0324	1900	B
Manganese	.0195	.0491	.105	.143	1680	C
Aluminum	.168	.203	.236	.252	1163	D

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A. R.R. Hultgren, etal, "Selected Values of the Thermodynamic Properties of Binary Alloys", Amer. Soc. for Met., Metals Park, Ohio, 1973.

B. J.P. Regert, A. Vermande, I. Ansara, High Temp.-High Pres., 5, 1973, page 231.

C. G.I. Batalin, V.S. Sudavtsova, Izv. Akad. Nauk. SSSR, Neor.Mater., 11, 1975, page 1782.

D. S.C. Schaefer, U.S. Bureau of Mines, Rep.Invest., RI 7895, 1974, 15 pp.

3.2 Reactant Feed Systems

Both the sodium system and the $SiCl_4$ system, as designed and costed during Phase I, are sufficient for use in the 1000 MT/year analysis for silicon production. The main difference between the reactant systems for a recycle operation (1000 MT/year Si) and the Phase II experimental verification is the source of the reactant feed materials. During Phase II, the reactants will be purchased and maintained in drums (sodium system) and a holding tank ($SiCl_4$ system) for testing purposes. However, for a recycle-type operation to produce 1000 MT/year of silicon both the sodium and $SiCl_4$ materials are supplied to the respective injection system from recycle operation. The sodium is obtained from electrolysis of the NaCl by-product, while the Cl_2 from the electrolysis is utilized to chlorinate a silicon-bearing material to produce $SiCl_4$. The specific components (e.g. pumps, piping, flow control, etc.) of the reactant feed systems will be identical to those specified for the Phase II test system. The cost information for the Phase II feed systems will be factored into the economic analysis for the 1000 MT/year case.

3.3 Plasma Reactor Analysis

Since the only silicon production level to be analyzed under Task 5 is 1000 MT/year, the design and costing data generated for the plasma reactor during Phase I will be sufficient for the economic evaluation of Task 5. The present reactor design is capable of producing the 125 kg/hr of silicon that equates to the 1000 MT/year requirement.

3.4 Silicon Product Collection

Due to the uncertainty of the method for silicon crystal growth (single crystal or sheet technology) that will be necessary for the 1980 goal (1000 MT/yr), the silicon collection subtask has been eliminated in Task 5 for the present analysis.

3.5 Electrolysis System

Several base case conditions have been determined for the recycle of NaCl from the production of 1000 metric ton of silicon/year. The sodium chloride will be separated into its elements via electrolytic dissociation. The sodium can be returned to the silicon production process directly and the chlorine will be used to produce silicon tetrachloride.

As reported previously, the theoretical material requirement is 0.86 lbs. of Cl_2/lb. $SiCl_4$.[4] Therefore, 1634 lb/hr of chlorine will be required to produce 1900 lb/hr of $SiCl_4$. The design bases to date are as follows:

-- 1640 lbs/hr of Cl_2 and 1061 lb/hr of Na
-- Commercial grade sodium can be used.
-- Downs cell design will be used.[5]
-- Raw material can be used as received from the process.

Electrolysis

-- Current efficiency will average 80%.[6]
-- Cell capacity is 1420 lb Na/day (22 hrs).[7]

Economic Basis

-- 1975 Capital Cost
-- January 1975 cost index

Data taken from the literature shows a range of 4.8 kwh/lb of Na[7,8] to 7.5 Kwh/lb of Na[6] using the Downs cell. The three major producers of metallic sodium in the United States (E.I. DuPont, Ethyl Corp., RMI) have been contacted and operating data requested and/or conformation of the data published in the literature. The initial response to the request has been negative because of fear of revealing confidential information. However, in each case, the contact person has agreed to determine what, if any, information can be released. In addition to operating data, each of the producers were asked for a typical analysis of their product and current selling prices.

A preliminary material balance has been completed and an energy balance is being studied. The process flow diagram is based on producing 1640 lb/hr of chlorine and receiving from the silicon production process 2338 lbs/hr of sodium chloride.

Process Flow Diagram

Figure 3.1 presents a preliminary flow diagram for proposed recycle process of NaCl for the electrolytic production of Na and Cl_2.

3.6 $SiCl_4$ Production

During the quarter, emphasis for this subtask was placed in the area of soliciting operating and process data from various $SiCl_4$ producers that have been identified. In addition, product price and product purity information was also assembled. A meeting was held with Van DeMark Chemical Co. in Lockport, N.Y. to obtain information on the Van DeMark process for $SiCl_4$ production. This process involves chlorination of a silicon carbide feedstock. The information exchange resulted in verbal descriptions of the process and the major process vessels.

Discussions were also conducted with Cabot Corporation regarding Cabot's $SiCl_4$ production processes. These processes include the chlorination of silica-carbon mixtures and the hydro-chlorination, $HCl_{(g)}$, of metallurgical grade silicon (m.g. Si). The operating and process information requested is undergoing legal review at Cabot to assessand protect proprietary information.

Based on the information obtained to date, there are three direct silicon tetrachloride production processes which can be classified according to the feedstock. These processes are (1) SiC chlorination, (2) SiO_2/C chlorination, (3) m.g. Si chlorination. Either Cl_2(g) or HCl(g) as the chlorinating agent can be used in all chlorination processes.

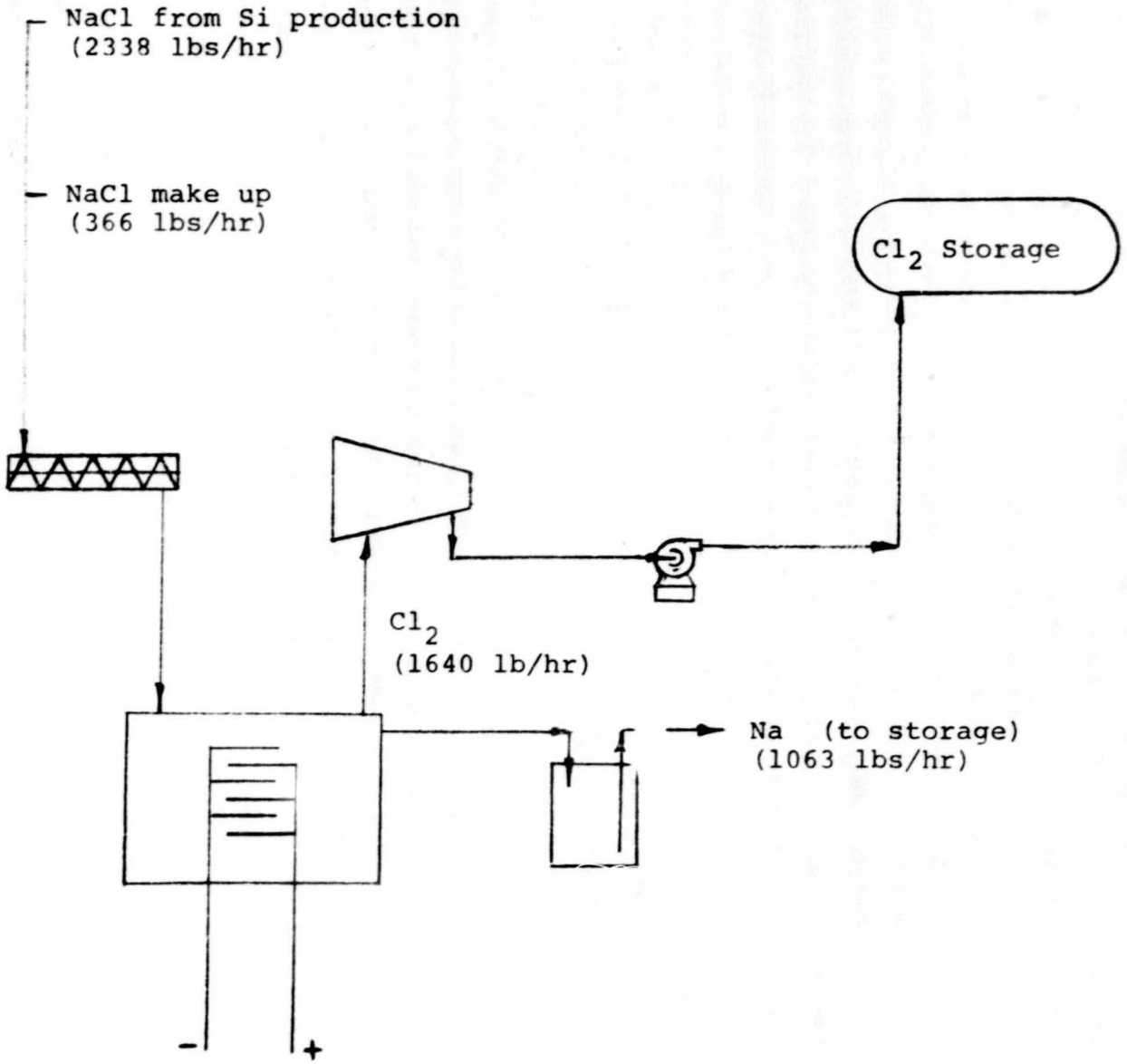

Fig. 3.1 -- Process Flow Diagram for NaCl Electrolysis System

1000 and 1600°K and for initial moles of SiO_2 and C of 1.0 and 2.0 respectively a minimum occurs in the energy requirement at approximately 2.0 moles of chlorine. This minimum increases with increasing temperature from 0.34 to 1.11 kw-hr/lb of Si.

Complex equilibria calculations were carried out in the Si-C-Cl system in order to determine the theoretical materials and energy requirement in the SiC chlorination process. The results of the calculations show that the yield, i.e. mols $SiCl_4$/mol SiC, is unity at a Cl_2/SiC ratio of 2.05 in the temperature range between 1000 and 1600°K. Under these conditions the theoretical materials requirements are 0.86 lbs Cl_2/lb $SiCl_4$ and 0.24 lbs SiC/lb $SiCl_4$. The overall reaction is exothermic in the temperature range considered. Consequently, the theoretical energy requirement is zero.

During the upcoming quarter, costing of the major equipment items for $SiCl_4$ production based on the Van DeMark process will be completed and factored into the process economics analysis for the 1000 MT/year of silicon.

3.7 $SiCl_4$ Purification

As envisioned in the recycle-type process to produce silicon, the $SiCl_4$ produced by chlorination of a silicon-bearing material (see Section 3.6) will probably require purification prior to use in the arc-heated reactor. This purification step is planned to involve distillation of the raw $SiCl_4$. The $SiCl_4$ purification process is being analyzed as part of Task 5 in addition to establishing the operating parameters and system requirements based on the process design format of Lamar University. Based on the design data generated, such items as the $SiCl_4$ purification flowsheet, equipment costs, and economic analysis will be integrated along with similar data from other system processes (i.e., chlorination, electrolysis, etc.) into the overall economic analysis for silicon production.

Silicon tetrachloride is also a major by-product of trichlorosilane and zirconium production. The former process involves the low temperature chlorination of m.g. Si with HCl(g), while the latter process includes a step in which zirconium silicate is chlorinated with Cl_2(g). A summary of $SiCl_4$ production methods along with other relevant process information has now been obtained from Van DeMark Chemical Co. to carry out a process design analysis for $SiCl_4$ production using SiC and Cl_2 as the feedstocks. Price and purity information on $SiCl_4$ produced as a by-product of $ZrCl_4$ production has been obtained from Teledyne-WahChang and is also shown in Table 1.

A preliminary process design analysis has been completed for $SiCl_4$ production based on the process and information obtained from Van DeMark Chemical Co. This process is based on the chlorination of silicon carbide to produce $SiCl_4$. Included in the preliminary design analysis are the following areas (which are patterned after the Lamar University format):[3] 1) base case conditions, 2) material and energy requirements, 3) preliminary process flow sheet, 4) types and sizing of process equipment, and 5) materials of construction. Since Van DeMark's current production capacity is ~10 million pounds/year of $SiCl_4$, their operating information and equipment had to be scaled-up to meet the $SiCl_4$ requirements for the Westinghouse process producing 1000 MT/year of silicon.

In addition to the information solicited from the various $SiCl_4$ producers, additional thermochemical calculations were made for both the SiC chlorination (Van DeMark) and the SiO_2-C chlorination (Cabot) processes to determine theoretical materials and energy requirements. The theoretical materials requirement for the chlorination of silica-carbon mixtures was presented in the previous Quarterly Report.[1] Theoretical energy balance calculations were carried out for the chlorination of SiO_2 - carbon mixture (Cabot process) based on the complex equilibria solutions in the Si-O-C-Cl systems. These calculations show that in the temperature range between

Table 3.2 - Summary of $SiCl_4$ Production Methods and Supplier Information

Process Classification	Producers Identified	Price	Purity/Analysis	Approx.Yearly Production
Chlorination of SiC	Van DeMark Chemical Co.	40¢/lb.	C.P. Grade % Free Cl 0.003** % Fe 0.00001 % Ti 0.00001 % V 0.000008 P(ppb) 15 B(ppb) 6	~10 million lb./yr
Chlorination of SiO_2 -carbon mixtures	Cabot Corp.	*	*	*
Chlorination of met.grade silicon	Cabot Corp.	*	*	*
$SiCl_4$ as a by-product from $ZrCl_4$ process	Teledyne-Wah Chang	22¢/lb.	Tech. Grade Fe ≤ 1 ppmw Free Cl ≤ 125 ppmw Ti ≤ 20 ppmw Al ≤ 2 ppmw Zr ≤ 20 ppmw V ≤ 1 ppmw Cu ≤ 1 ppmw	~20 million lb/yr
$SiCl_4$ as a by-product from tri-chlorosilane process	Union Carbide	46¢/lb.	Tech. Grade 99% pure, no analysis available	Variable
	Dow Corning	26¢/lb.	Tech. Pure 99.4% no analysis available	Variable

** Percentage, %, molar

* Information not on hand

During the quarter, two reports were received from the CYM Engineering Co. that is conducting the $SiCl_4$ purification analysis. These reports presented the preliminary process design analysis for $SiCl_4$ purification via distillation for two separate design cases (Cases A and B). Three cases are being analyzed for the $SiCl_4$ purification: Case A - purification of $SiCl_4$ based on operating conditions from trichlorosilane distillation, Case B - $SiCl_4$ purification by distillation for removal of p- and n-type impurities in separate columns, and Case C - $SiCl_4$ purification via distillation for n-type impurity removal in a single column. All three cases and the respective analyses are based upon 1) feedstock of $SiCl_4$ from the Van DeMark process and product purity and 2) providing sufficient purification of the $SiCl_4$ equivalent to 100 ohm-cm silicon material. Both reports (Cases A and B) included data for 1) base case conditions, 2) preliminary flowsheet, 3) material and energy requirements, 4) list of major process equipment, and 5) preliminary costs for the process equipment. The preliminary capital costs of the installed equipment based on the CYM analysis are as follows: Case A - $356K and for Case B - $453K. Case C is still in progress at CYM. These costs, in addition to energy costs, material costs, and other indirect costs will serve as input data to the overall economic analysis for the 1000 MT/year silicon production.

3.8 Scaling Parameters

Due to the redirection of Task 5, this subtask has been eliminated since it is not required for the 1000 MT/year production case.

3.9 Effluent Separation

During the quarter, additional analyses and preliminary design work were accomplished on the NaCℓ cyclone for effluent separation. This cyclone method for separation of the co-product NaCℓ from the arc

heater gases is being evaluated as an alternative to the more expensive, dual condensers that were originally proposed as the principal method for salt separation.[2]

This alternate system is shown in Figure 3.2 and consists primarily of a cyclone for separating the liquid NaCl from the gas stream, a NaCl collector vessel, and a gas scrubber. In operation, particulate NaCl at ambient temperature is injected into the high temperature by-product stream as it exits the silicon separating cyclone. This injected NaCl (s) lowers the gas stream temperature to below the condensation point of the gaseous NaCl, and provides nucleation sites for NaCl condensation and growth so that the particles can be efficiently removed from the gas stream by the cyclone. The separated liquid NaCl then runs downward along the cyclone walls and into a collection vessel.

The co-product NaCℓ(v) is produced during the reduction reaction at a rate of 0.21 kg/s which is based on a silicon production rate of 91 kg/hr (200 lb/hr). The NaCℓ particles will be injected at a rate of 0.42 kg/s for cooling the NaCℓ(v). An analysis of this system was performed to determine the thickness of the frozen NaCℓ skull that lines the NaCℓ cyclone wall. In order to determine this thickness, two separate heat transfer rates are required: 1) the rate of convective transfer from the hot gases to the cyclone wall and 2) the rate of heat transfer from the salt droplets to the cyclone wall upon impact.

The heat from the salt droplets was analyzed as follows, on the basis of a 200 lb/hr production rate of silicon:

Salt-gas stream temperature (by heat balance) = 1372°K
NaCℓ enthalpy @ 1372°K = 16.274 kcal/mole
Cyclone wall temperature = 1072°K
NaCℓ enthalpy @ 1072°K = 11.366 kcal/mole

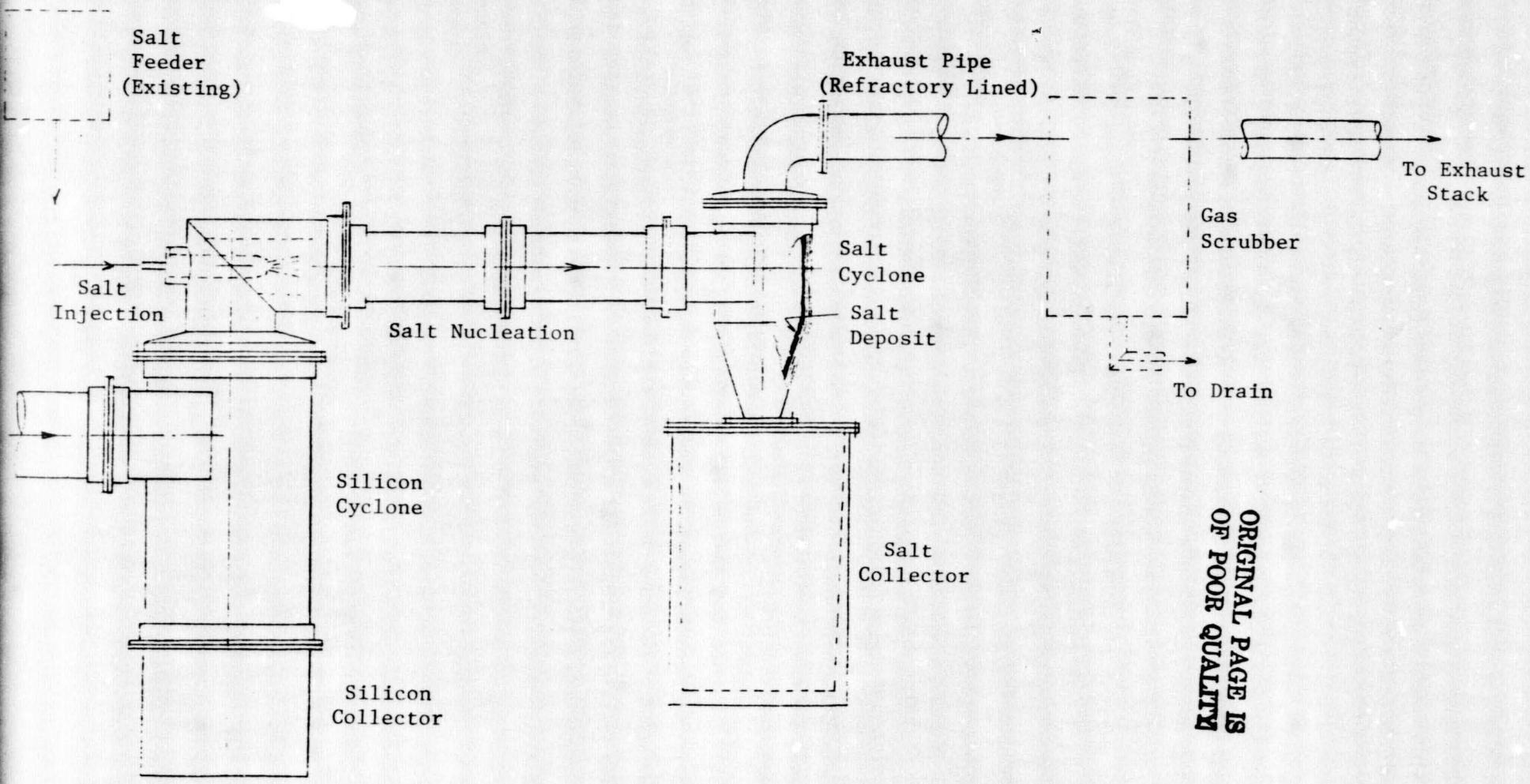

Figure 3.2 - **Salt Cyclone Concept for Effluent Separation**

NaCℓ molecular weight = 58.44

Heat released by droplets to wall = 84 Kcal/Kg

Total NaCℓ flow rate = 0.6313 kg/sec.

Rate of heat release to cyclone wall = 222 kW

Cyclone wall area = 1.632 m^2

Rate of release/unit area = 136 kW/m^2

The above analysis assumes that all of the NaCℓ(v) is condensed to a liquid and collected on the cyclone wall.

The convective heat transfer from the hot gases to the cyclone wall is obtained after determining the film coefficient (h). This calculation is based on the assumptions that the gas velocity in the cyclone is equal to the velocity in the inlet duct and that the characteristic dimension, D, equals the cyclone diameter (D=0.5m). The duct dimensions are width = 0.76m and height = 0.20m. Therefore, the cross sectional area of the duct equals $0.0155m^2$. Based on the mass flow rate of gas ($\dot{m}$) and the gas viscosity (μ), the Reynolds number can be calculated

$$Re = \frac{D\,\dot{m}}{\mu\,A} = 30,564 \qquad (1)$$

where $\dot{m}$ = 0.379 kg/sec

μ = 4.0×10^{-5} pa-sec

Using the Nusselt-type equation for the forced convection, turbulent region:[9]

$$\frac{h\,D}{k} = 0.23\ (Re)^{.8}\ (Pr)^{.33} \qquad (2)$$

where Pr = 0.38

k = 0.4215 $W/m^2°K$

D = 0.5m

thus, h = 54.58 $W/m^2°K$

therefore, with the film coefficient, h, determined; the convective heat

transfer can be evaluated for the Cℓ cyclone design.

Equating the rate of heat loss from the gas, q_ℓ, to the rate of convective heat transfer, q_c, the convective heat transfer parameters are obtained:

$$q_\ell = \dot{m}\, c_p\, (T_{in} - T_{out}) \tag{3}$$

and

$$q_c = h\, A\, (Tm - Tw) \tag{4}$$

where Tm = mean temperature
Tw = wall temperature

since

$$Tm = \frac{T_{in} + T_{out}}{2} \tag{5}$$

therefore, setting $q_\ell = q_c$ yields

$$T_{out} = \frac{T_w + T_{in}\left(\frac{\dot{m}\, c_p}{h\, A} - \frac{1}{2}\right)}{\frac{\dot{m}\, c_p}{h\, A} + \frac{1}{2}} \tag{6}$$

where Tw = 1072°K , T_{in} = 1372°K
Tm = 1288°K , T_{out} = 1204°K

and q_c = 19.24 kW

thus, the heat transfer per unit area becomes

$$q/m^2 = 11.789\ kW/m^2$$

Since the two heat transfer rates have been calculated, the NaCl thickness, ℓ, on the cyclone walls can be determined using the heat transfer equation for conduction, q_{cd}:

$$q_{cd} = \frac{k_{NaCl} A}{\ell} (Tw - T_o) \qquad (7)$$

Upon solving equation (7) for ℓ yields:

$$\ell = \frac{k_{NaCl} A}{q_{cd}} (Tw - T_o) \qquad (8)$$

where T_o = 298°K = outer NaCl liner surface temperature.

Tw = 1072°K = inner NaCl liner surface temperature.

and k_{NaCl} = 2.474 W/m-sec °K

thus, ℓ = 0.013 m (0.511 inches)

From this heat transfer analysis, it can be concluded that 1) the heat transfer is dominated by particle impingement and 2) the NaCl liner thickness (skull) is reasonably thin on the cyclone wall.

In areas where heat transfer rates are low, such as the top cover surface and the exit nozzle, solid salt thickness will be much greater than calculated above if these surfaces were water-cooled metal. Hence, it is planned to cover these surfaces with an insulating material such as a combination of graphite and graphite felt to prevent excessive buildup. The outlet extension will be of solid graphite. All graphite parts will be silicon carbide infused or coated to limit erosion. The effluent outlet and conduit leading to the downstream gas scrubber will be constructed of stainless pipe or tubing with an external layer of insulation to prevent excessive buildup of condensing materials on the inner surface.

As shown in Figure 3.3, the collector vessel is water cooled and is sized to collect 5000 lb. of salt or the equivalent of a one-hour running time at a silicon production rate of 200 lb/hr. The inner liner is separable from the outer shell to facilitate exchange of liners, if required.

Since the present method for effluent treatment requires water for scrubbing the gas stream, it was necessary to determine the rate of water vapor diffusion upstream to determine whether product contamination could result. A simple diffusion calculation, based on the configuration shown in Figure 3.4, was performed.

At Station 1 (see Figure 3.4), assume a stream of flowing hydrogen and argon (4:1 molar proportion) with the salt largely removed. A concentration of water vapor at Station 2 is assumed and the stream velocity necessary for the concentration of water vapor at Station 1 to fall below a specified minimum level (e.g., a partial pressure of 10^{-6} atm) is determined. For the flux of water vapor by diffusion to be balanced by the macroscopic transport of water vapor we have:

$$-D \frac{dC_1}{dx} = C_1 U \qquad (1)$$

For simplicity, the velocity U is assumed constant; the duct wall is adiabatic and the mixture diffusion coefficient for species 1 through the mixture is represented as:[10]

$$D = \frac{1-X_1}{\sum_{j=2}^{n} \frac{X_j}{\mathcal{D}ij}} \qquad (2)$$

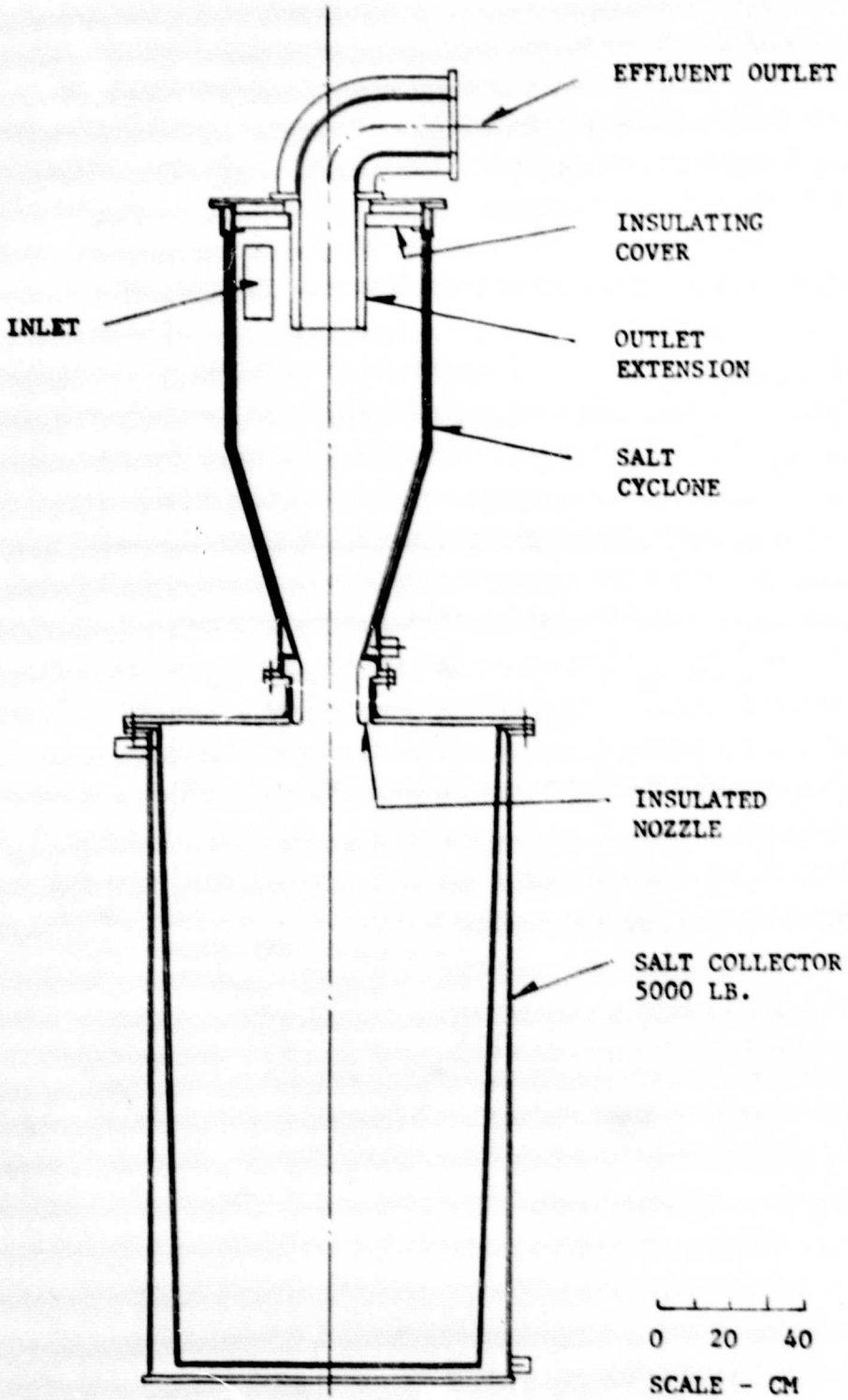

Figure 3.3 - NaCl Cyclone Separator and Salt Collector

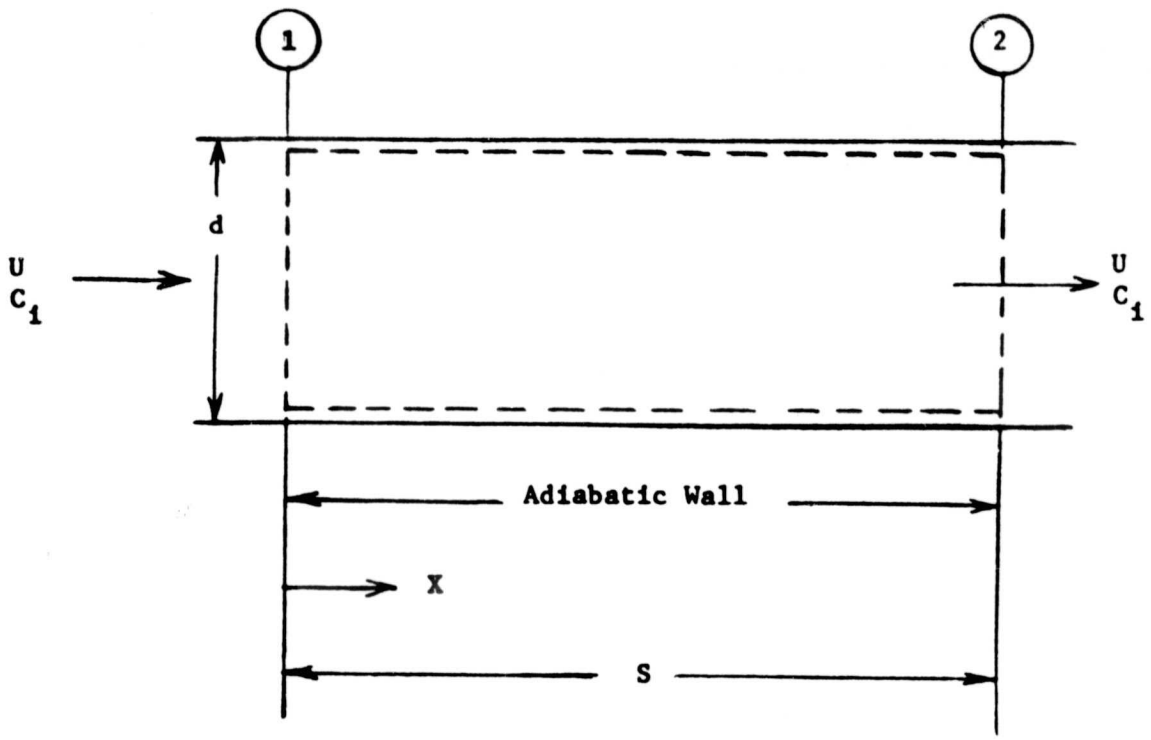

Figure 3.4 - **Schematic of Diffusion Model**

The binary diffusion coefficients $\mathcal{D}_{ij}$ are obtained by data and methods provided in Perry's Chemical Engineering Handbook.[9] The exponential characteristic concentration length is D/U. Using these relations and data at three representative temperatures, minimum velocities and mixture diffusion coefficients were determined and are shown in Table 3.3. The velocity is such that the concentration of water vapor at Station 1 is 6 orders of magnitude below that at Station 2 which is 1 meter downstream. Higher velocities will further reduce the upstream concentration. Since these velocities are 2 to 3 orders of magnitude below those existing in the proposed system, water vapor diffusion is not considered to be a contamination source. As represented in the November-December quarterly,[1] the mass diffusion attributed to macroscopic turbulence can be represented by:

$$D = 0.002 \; Ud \tag{3}$$

Assuming turbulence to be the dominant diffusion transport mechanism, it can be shown that the characteristic concentration length, λ, is:

$$\lambda = 0.002d \tag{4}$$

Assuming this exponential characteristic length, the concentration one meter upstream for any reasonable duct diameter (i.e., 0.01m to 1m) is undetectably small and independent of velocity. One can conclude that water vapor contamination of the reactor system cannot occur under normal operating conditions as a result of diffusion alone.

Nomenclature List:

C_i	concentration of species "i" with i = 1 for water vapor
d	duct diameter
D	mixture diffusion coefficient
$\mathcal{D}_{ij}$	binary diffusion coefficient for species "i" and "j"
x	axial distance
U	axial velocity
X_i	mole fraction of species "i"

Table 3.3 - Mixture diffusion coefficient, D, and minimum flow velocity, U, as a function of stream temperature for 10^{-6} water vapor concentration in a 1 meter length.

T (° K)	D (m^2/s)	U (m/s)
800	3.36×10^{-4}	0.46×10^{-2}
1000	4.90×10^{-4}	0.68×10^{-2}
1200	6.65×10^{-4}	0.92×10^{-2}

3.10 Auxiliary System Requirements

This subtask has been eliminated based on the rescoping of Task 5.

3.11 Safety and Environmental Conformance

This subtask has been eliminated since it does not directly serve an economic analysis aimed at projecting a cost for producing silicon ($/kg Si).

3.12 Process Economics

As the design information and data are generated during the process engineering analysis, the appropriate cost data will be forwarded to the economic analysis to determine fixed capital, direct, indirect, and manufacturing costs based on producing 1000 MT of silicon per year. The format for this economic analysis will follow the method presented by Lamar University[3] for consistency and comparison purposes. This analysis will determine the cost of producing the 1000 MT/year of silicon in reference to the DOE/JPL cost goal of $10/kg of silicon.

3.13 Design Review

A design review will be held jointly with JPL personnel to review the design and status of the Phase II program. As part of the review, discussions of the differences between the Phase II test system and that evaluated for recycle-production process (1000 MT/year) in Task 5 will be conducted. A design review is scheduled for late October, 1977 with JPL.

4. CONCLUSIONS

- Based on preliminary analyses, the NaCl(v) effluent (by-product) produced during the reaction can be effectively cooled by injecting additional NaCl particles into the gas stream.
- Analysis has indicated that the NaCl cyclone can be designed using the skull wall concept and, that the equilibrium thickness of NaCℓ on the cyclone wall is on the order of 0.5 inch.
- Investigations have indicated that NaCl electrolysis to produce sodium and chlorine for a recycle-type silicon production process will utilize state-of-the-art technology.
- Purification of the $SiCl_4$ produced for a recycle silicon process will be obtained utilizing state-of-the-art distillation technology (based on the CYM Engineering Co. study).
- Based on a calculation, water vapor diffusion from the gas scrubber is not expected to produce product contaimination under normal operating conditions.
- Based on the vendor information received, the Van DeMark Chemical Co. process for $SiCl_4$ production was selected as a base in the process and economic study of Task 5.
- Based on thermodynamic analysis, the theoretical material requirements for the chlorination of silicon carbide to produce $SiCl_4$ is approximately stoichiometric, i.e. mols $SiCl_4$/mol SiC is unity at a $Cℓ_2$/SiC ratio of 2.05 in the temperature range of 1000 - 1600°K.
- As a result of the CYM Engineering Co. analysis for $SiCl_4$ purification via distillation (Case A), a preliminary installed equipment cost of $356K has been established.

5. PROGRAM STATUS

5.1 Present Status

The Task 5 effort is progressing on schedule and will be completed in the upcoming month, as shown in Table 5.1

5.2 Future Activity

- Complete the Task 5 effort, i.e. process analysis and economics.
- Continue the System Purity Analysis effort.
- Conduct a design review for Task 5 with JPL in late October.
- Continue the effort to assess alternative effluent separation techniques for the co-product NaCl (v).

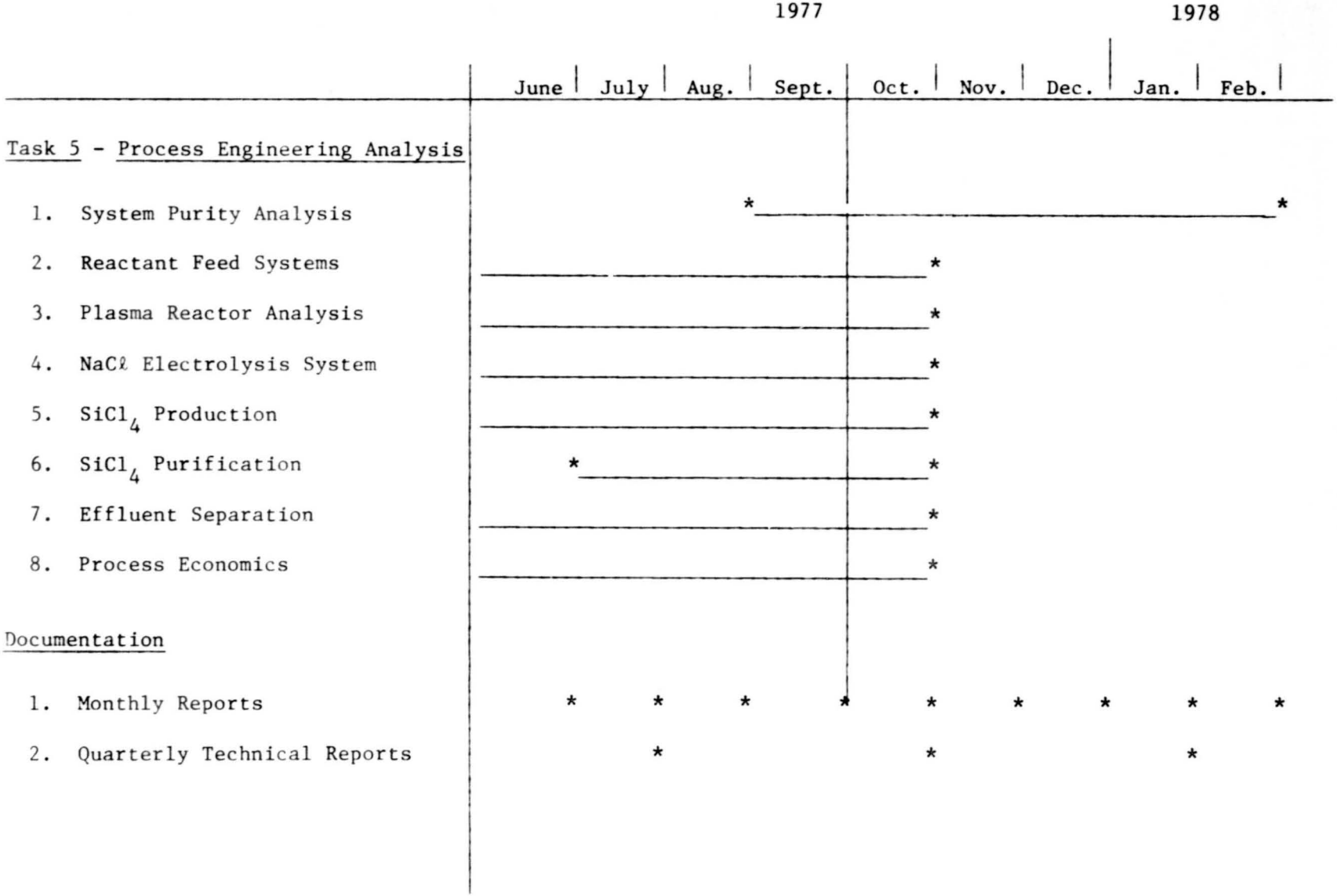

Table 5.1 - Milestone Chart for Task 5: Process Engineering Analysis

6. REFERENCES

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